

POTENTIAL TECHNOLOGY TRANSFERS OF RESEARCH ON LOW-TEMPERATURE  
CARBON MONOXIDE - OXYGEN RECOMBINATION CATALYSTS

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SUMMARY

Results from research on catalytic recombination of CO-O<sub>2</sub> for stable closed-cycle operation of CO<sub>2</sub> lasers hold much promise for a variety of technology transfers. Expansion of CO<sub>2</sub> laser remote sensing applications toward chemical detection and pollution monitoring would certainly be expected. However, the catalysts themselves may be especially effective in low-temperature oxidation of a number of chemicals in addition to CO. It is therefore of interest to compare the CO-O<sub>2</sub> catalysts with chemical systems designed for chemical sensing, air purification and process catalysis. Success in understanding the catalytic mechanisms in the recombination of CO-O<sub>2</sub> could help to shed light on how catalyst systems operate. New directions in low-temperature oxidation catalysts, coatings for chemical sensors and sorbents for air purification could well emerge.

INTRODUCTION

There are a number of applications for CO-O<sub>2</sub> recombination catalysts. An important one is the achievement of long-term, closed-cycle operation of CO<sub>2</sub> lasers. The lasers are used for remote-sensing applications such as observing and predicting atmospheric behavior. The ability to understand catalyst performance and to control frequency stability is critical. CO<sub>2</sub> can dissociate in the laser discharge to CO and O<sub>2</sub>. The loss of CO<sub>2</sub> results in a corresponding loss of laser power. The buildup of O<sub>2</sub> can cause discharge instabilities. A catalyst is needed to facilitate recombination of the CO-O<sub>2</sub>. It is critical that the mechanisms involved in the catalytic recombination be understood. The challenges are multifold and include the need for studies of the catalytic process as well as the physical and chemical properties of the catalyst. An excellent review of approaches toward efficient recombination catalysts appeared in the proceedings of a workshop held at the NASA Langley Research Center in 1986 (ref. 1). A review of recent advances was presented in 1988 (ref. 2).

Pt/SnO<sub>2</sub> appears to be the most promising catalyst system for the recombination of CO and O<sub>2</sub> in CO<sub>2</sub> lasers (ref. 3). A systematic study of Pt, Pd/SnO<sub>2</sub> catalysis has been underway for several years. There are many parameters including catalyst preparation, catalyst surface area, effect of CO<sub>2</sub> concentration, catalyst pretreatments, catalyst distribution and quality control of test procedures, to mention several. Considerable progress has been made toward high activity systems for combining CO and O<sub>2</sub> to form CO<sub>2</sub> in high powered lasers. This will be discussed at the International Conference on CO Oxidation Catalysts for Long-Life CO<sub>2</sub> Lasers in October 1989 at the NASA Langley Research Center, Hampton, VA.

As pointed out during the international conference in 1986, the immediate United States interest in the development of pulsed CO<sub>2</sub> lasers is for the NASA Marshall Space Flight Center Windstat program (involving the measurement of wind) (ref. 4). However, it was mentioned that the potential for technology transfer to industrial, medical, defense and other research applications is significant. Industrial process control, laser ranging, communication, frequency stability and reliable long-term unattended operation were mentioned as being most important. United Kingdom

interests relate heavily to military applications; however, there is also a policy of technology transfer to industry (ref. 5).

The purpose of the present paper is to more specifically outline the potential technology transfers from the research on low-temperature CO-O<sub>2</sub> recombination catalysts. Major areas discussed include:

- Remote sensing
- Chemical sensors
- Air purification
- Process catalysis.

## REMOTE SENSING

An appreciation of the utility of lasers in meteorology, and earth and atmospheric remote sensing can be obtained by reviewing the proceedings of a recent conference on the subject (ref. 6). The titles of the sessions reflect the scope:

- Advances in laser technology for remote sensing
- Laser remote sensing for meteorology applications
- Laser remote sensing for surface applications
- Laser remote sensing of trace species
- Laser remote sensing of velocity fields.

Titles in the session on trace-species sensing follow:

- Remote active spectrometer
- Measurement of atmospheric trace species and rocket fuels using CO<sub>2</sub> lidars
- Development of an active imaging system and its application to the visualization of gas clouds
- Multiwavelength and tripled CO<sub>2</sub> lidars for trace gas detection
- Analysis of laser diagnostics in plumes
- CO<sub>2</sub> laser photoacoustic detection of trace toxic compounds in the ambient air
- Stratospheric ozone measurements with a ground-based, high power lidar
- CO<sub>2</sub> DIAL measurements of toxic gases.

Chemical analysis at a distance is of special interest for many reasons. Recent progress in the possibility of a chemical warfare treaty highlights the need for chemical monitoring and verification procedures. The war on drugs could benefit from stand-off sensors to locate and identify organic vapors from suspected drug-processing facilities. Also, many environmental situations require a variety of chemical sensors including stand-off systems. Use of differential absorption lidar for pollution mapping is a good example. Table I lists molecules of interest in air pollution and their absorption wavelengths corresponding to wavelegths of line-tunable CO<sub>2</sub> lasers.

Achievement of long-term, closed cycle operation of CO<sub>2</sub> lasers should significantly expand the use of remote sensing especially in the detection, identification and monitoring of pollutants.

## CHEMICAL SENSORS

The first  $\text{SnO}_2$  semiconducting gas sensor was marketed over two decades ago for the detection of combustible gases. Applications have been extended to the sensing of ammonia, hydrogen sulfide, thiols, ethanol, hydrogen, CO, arsine, acetic acid and other compounds. A recent review on the development of  $\text{SnO}_2$  sensors is available (ref. 8), as well as an outline of what was published on conductometric sensors during the 1985-1987 period (ref. 9). The mechanism of detection in air is usually a catalytic oxidation at the surface of the oxide inducing an increase in conductance. The operating temperature for a particular sensor would most likely be found in the range of 200-400°C. Recent advances relate to selectivity and include a combustible gas detector having insensitivity to reductive gases (ref. 10). Several patents (mostly to Japanese companies) have appeared for CO detection using semiconducting oxides.

$\text{SnO}_2$  is the most frequently used material for semiconducting gas sensors. Few other materials have been put into practical use. The sensitivity of the sensor for CO can be improved significantly by adding Pt or Pd; silanization with trichlorosilane enhances the selectivity for  $\text{H}_2\text{S}$  (ref. 9). There appears to be more interest at the present time in studying  $\text{SnO}_2$  to increase its performance rather than to search for new materials. Increasing selectivity, sensitivity, reliability and long-term stability are the goals.

Applications of  $\text{SnO}_2$  gas sensors include:

- Toxic gas detection ( $\text{CO}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ , etc.)
- Combustion monitoring
- Gas-leak detection
- Air quality monitoring
- Fermentation control
- Ventilation control
- Fire detection ( $\text{CO}$ )
- Breath analyzer (alcohol).

These and some new applications such as detection of odors (e.g., in testing for freshness of foods) are discussed briefly in reference 8.

The  $\text{SnO}_2$  and other catalysts emerging in the research on  $\text{CO-O}_2$  recombination for the  $\text{CO}_2$  laser application should be considered candidates for semiconducting oxide sensors and vice versa. A low-temperature  $\text{SnO}_2$  system developed in the laser work could dramatically expand the utility of semiconducting oxides in chemical sensing.

## AIR PURIFICATION

Catalysts for removal of CO from air at room temperature are commercially available. Hopcalite, a co-precipitate of oxides of manganese and copper, is a classic example. As pointed out by Sampson and Gudde (ref. 11), the main difference between CO oxidation for air purification and for laser control lies in the gas composition. The CO and  $\text{O}_2$  concentrations are much higher and the  $\text{CO}_2$  concentrations much lower in the air purification application than in the laser recombination one. However, the operating requirements are very similar.

It is of interest to compare the CO-O<sub>2</sub> recombination catalysts with other systems known to react with CO. For example, the current U.S. Department of Defense sorbent for air filters in chemical defense is whetlerite. This is an activated charcoal which has been impregnated with a mixture of copper, silver and chromium. It functions through a combination of physical adsorption and chemisorption. Descriptions of some of the chemistry and characteristics of whetlerite are available (ref. 12, 13). It is known that CO is oxidized at room temperature in air using whetlerite (ref. 14, 15). The activation energy for the oxidation was estimated to be 14.6 kJ mol<sup>-1</sup> (ref. 16). The oxidation of CO has also been proposed as a nondestructive test for predicting the residual chemical life of whetlerite (ref. 17, 18). The chemical reactivity of whetlerite involves both hydrolysis and oxidation. However, the mechanisms are complicated; complete details have not been worked out. Several analogies can be drawn between the Pt/SnO<sub>2</sub> oxidation of CO in the laser application and the chemisorption processes in air purification using whetlerite. It is pertinent to compare the proposed reaction mechanisms for the respective systems. Success in understanding the catalytic process in the recombination of CO-O<sub>2</sub> could help to shed light on how other oxidation catalysts work including whetlerite.

New or modified sorbents for air purification could emerge as a result of the research on CO-O<sub>2</sub> recombination catalysts. Low temperature oxidation catalysts for CO have been investigated with other toxics for air purification. (ref. 19).

## PROCESS CATALYSIS

A product review on process catalysts showed that nearly every segment of the catalyst business is growing (20). The value of catalysts consumed in pollution abatement uses this year is expected to exceed the value of catalysts consumed in petroleum processing. However, the physical volume of catalysts used in pollution control is actually quite small because of the high activity and cost of Pt and other metals of the Pt group used as catalysts. Automotive catalysts accounted for 43% of all U.S. consumption of platinum group metals in 1987. A major problem is still the stability of the noble-metal catalysts and the catalyst supports (21). Environmental catalysts should lead value growth among other catalysts into the next century, however, research is underway to find catalysts that are less expensive than the noble metal ones.

It has been estimated that almost 25% of the total production volume of the top 20 chemicals worldwide depends upon selective oxidation catalyzed by solid metal oxides (22). The most selective catalysts contain a cation with an empty or full outermost *d* orbital. This includes Sn(IV) which has a 4*d*<sup>10</sup> orbital.

The work on Pt/SnO<sub>2</sub> for CO-O<sub>2</sub> recombination should lead to new insights on catalytic oxidation mechanisms as well as materials which may be relevant to various aspects of process catalysis.

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TABLE I. - ABSORPTION WAVELENGTHS FOR MOLECULES OF INTEREST IN AIR POLLUTION STUDIES (REF. 7)

<u>Compound</u>	<u>Wavelength</u>
Carbon Monoxide	4.709 4.776
Nitric Oxide	5.263
Sulfur dioxide	8.881 9.024
Ammonia	9.220
Freon-11	9.261
Ozone	9.505 9.508
Freon-113	9.604
Benzene	9.621
Methyl hydrazine	10.182
Ethyl mercaptan	10.208
Ethyl chloride	10.275
Ammonia	10.333
Ethylene	10.533
Sulfur hexafluoride	10.551
Trichloroethylene	10.591
1,2,-Dichloroethane	10.591
Hydrazine	10.612
Vinyl chloride	10.612
1,1-Dimethylhydrazine	10.696
Freon-12	10.719
Perchloroethylene	10.742
1-Butene	10.787
Perchloroethylene	10.834

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#### ACKNOWLEDGMENT

Part of this work was performed by the author as an American Association for the Advancement of Science (AAAS) Science and Engineering Environmental Fellow in the Office of Modeling, Monitoring Systems and Quality Assurance, U.S. Environmental Protection Agency, Washington, DC. The support of AAAS and the U.S. Environmental Protection Agency is gratefully acknowledged.







## Report Documentation Page

1. Report No. NASA CP- 3076		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle  Low-Temperature CO-Oxidation Catalysts for Long-Life CO <sub>2</sub> Lasers				5. Report Date June 1990	
				6. Performing Organization Code	
7. Author(s)  David R. Schryer and Gar B. Hoflund, Editors				8. Performing Organization Report No. L-16797	
				10. Work Unit No. 584-01-31-50	
9. Performing Organization Name and Address  NASA Langley Research Center Hampton, Virginia 23665-5225				11. Contract or Grant No.	
				13. Type of Report and Period Covered Conference Publication	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546 Royal Signals and Radar Establishment Malvern, United Kingdom WR14 3PS				14. Sponsoring Agency Code	
15. Supplementary Notes  David R. Schryer, NASA Langley Research Center, Mail Stop 468, Hampton, Virginia  Gar B. Hoflund, University of Florida, Gainesville, Florida					
16. Abstract  Low-temperature CO-oxidation catalysts are necessary for closed-cycle pulsed CO <sub>2</sub> lasers as well as for other applications, including air purification. The papers presented in this volume discuss several such catalysts, including information on catalyst preparation, techniques for enhancing catalyst performance, laboratory and laser test results, and mechanistic considerations.					
17. Key Words (Suggested by Author(s))  CO Oxidation Catalysts CO <sub>2</sub> Lasers			18. Distribution Statement  Unclassified - Unlimited  Subject Category 36		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of pages 424	
				22. Price A18	